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THE COUPLED REPRESENTATION MATRIX OF THE PAIR HAMILTONIAN.(U)
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North Carolina University
Chapel Hill, North Carolina

1 January 1977

OFFICE OF NAVAL RESEARCH

Contract N00014-76-C-0816

Task No. NR 053-617

TECHNICAL REPORT NO. 1

The Coupled Representation Matrix of the Pair Hamiltonian

by

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Prepared for Publication

in the

Molecular Physics

University of North Carolina
Department of Chemistry
Chapel Hill, North Carolina 27514

January 1, 1977

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 1	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Coupled Representation Matrix of the Pair Hamiltonian		5. TYPE OF REPORT & PERIOD COVERED Interim
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Raymond P. Scaringe, Derek J. Hodgson, and William E. Hatfield		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0816
9. PERFORMING ORGANIZATION NAME AND ADDRESS The University of North Carolina Department of Chemistry Chapel Hill, North Carolina 27514		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-617
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE January 1, 1977 13. NUMBER OF PAGES 27
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release, Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Prepared for publication in Molecular Physics.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Exchange Coupling
Electron paramagnetic resonance
Magnetic Susceptibility
Spin Hamiltonian
Clebsch-Gordon coefficients
Wigner-Eckart theorem

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The evaluation of matrix elements in the spin Hamiltonian for a pair of exchange coupled metal ions is treated using the "total-spin" Hamiltonian through application of the Wigner-Eckart theorem.

The study of exchange coupled metal ions has been the subject of numerous studies employing a variety of physical and spectroscopic techniques. Electron paramagnetic resonance studies of crystalline dimeric complexes and highly doped single crystals containing pairs have been reviewed extensively[1-4].The magnetic susceptibility of dimeric complexes has also been the subject of several reviews[3,5-7], and a number of n.m.r. contact shift studies[8] of dimeric complexes have been reported. The interpretation of all such studies rests upon the determination of the parameters contained in the spin Hamiltonian of the pair. The evaluation of matrix elements then is a primary concern, and there are basically two ways in which to approach the problem. In the first method one takes advantage of the fact that the spins are coupled by taking linear combinations of single ion state vectors, $|S_1S_2M_1M_2\rangle$, so that the resulting wave functions are eigenfunctions of the total spin operators Σ^2 and $\Sigma_z(\Sigma_i = S_{1i}+S_{2i})$, but treats the problem completely in terms of single spin operators. In the second method one starts with the coupled representation state vectors, $|SM\rangle$, and transforms the Hamiltonian so that it contains only total spin operators. The generality of this method provides insight that is lacking in the first approach to the pair problem and also reduces the number of operator expressions required to evaluate the Hamiltonian matrix. To our knowledge, a full treatment of the general case using the "total-spin" Hamiltonian has not been reported. Thus, it is the purpose of this paper, to report the results obtained by the latter method through the application of the Wigner-Eckhart theorem.

I. The Pair Hamiltonian.

We assume that the pair Hamiltonian can be expressed as the sum of the two single ion spin Hamiltonian plus terms representing interactions between the two ions of the pair. This implies that the interaction terms are small compared to the crystal field splittings and will thus have a negligible effect on the single ion tensors. The general form of the pair Hamiltonian can then be written as follows:

$$H = H_1 + H_2 - 2J\underline{S}_1 \cdot \underline{S}_2 + S_1 \cdot \underline{D}_{e+d} S_2, \qquad (1)$$

where

$$H_i = \beta \underline{H} \cdot \underline{G}_i \cdot \underline{S}_i + \underline{S}_i \cdot \underline{D}_i \cdot \underline{S}_i + \underline{S}_i \cdot \underline{A}_i \cdot \underline{I}_i .$$

Eq. (1) assumes nothing about the relative orientation or form of the various tensors, and D_{e+d} can contain anisotropic exchange terms as well as the dipole-dipole contribution. The usual procedure for evaluating the matrix of (1) is to expand the total spin state vectors $|S,M\rangle$, in terms of the single spin state vectors, $|S_1S_2M_1M_2\rangle$, as follows:

$$|SM\rangle = \sum_{M_1M_2} C(S_1S_2S;M_1M_2M)|S_1S_2M_1M_2\rangle, \qquad (2)$$

where $C(S_1S_2S;M_1M_2M)$ is the Clebsh-Gordan coefficient, for which we have adopted Rose's[9] notation. Once the wave functions are in this form one can use (1) directly to evaluate matrix elements. While this process is straightforward, it is quite tedious, and the expansion in (2) must be found for each pair system characterized by different S_1 and S_2. It is possible to avoid the expansion in (2) by evaluating the matrix of (1) in the coupled representation, and to facilitate this process we have rewritten (1) as follows:

$$
\begin{aligned}
\mathcal{H} = {} & -J\{\underline{\Sigma}\cdot\underline{\Sigma} - S_1(S_1+1)-S_2(S_2+1)\} \\
& + \beta/2\{\underline{H}\cdot\underline{G}_\sigma\cdot\underline{\Sigma} + \underline{H}\cdot\underline{G}_\delta\cdot\underline{\Delta}\} + 1/2\{\underline{\Sigma}\cdot\underline{A}_1\cdot\underline{I}_1 + \underline{\Delta}\cdot\underline{A}_1\cdot\underline{I}_1\} \\
& + 1/2\{\underline{\Sigma}\cdot\underline{A}_2\cdot\underline{I}_2-\underline{\Delta}\cdot\underline{A}_2\cdot\underline{I}_2\} + 1/4\{\underline{\Sigma}\cdot\underline{D}_{e+d}\cdot\underline{\Sigma}-\underline{\Delta}\cdot\underline{D}_{e+d}\cdot\underline{\Sigma}\} \\
& + 1/4\{\underline{\Sigma}\cdot\underline{D}_\sigma\cdot\underline{\Sigma}+\underline{\Delta}\cdot\underline{D}_\sigma\cdot\underline{\Delta}\} + 1/2\underline{\Sigma}\cdot\underline{D}_\delta\cdot\underline{\Delta},
\end{aligned}
\tag{3}
$$

where $\underline{\Sigma} = \underline{S}_1+\underline{S}_2$, $\underline{\Delta} = \underline{S}_1-\underline{S}_2$, $\underline{G}_\sigma = \underline{G}_1+\underline{G}_2$, $\underline{G}_\delta = \underline{G}_1-\underline{G}_2$, etc. The state vectors $|S,M\rangle$ are eigenfunctions of the familiar total spin operators $\underline{\Sigma}\cdot\underline{\Sigma}$ and Σ_z, and matrix elements of the form $\langle S'M'|\Sigma_i|SM\rangle$, $(i = x,y,z)$, vanish for $S'\neq S$. Terms containing components of the less familiar vector operator $\underline{\Delta}$, however, follow the selection rule $S' = S$, $S\pm 1$, $S\pm 2$. The matrix elements of terms containing Δ_i $(i = x,y,z)$ can also be evaluated in the coupled representation. Much of what will follow then, will deal with finding the matrix elements of the Δ_i and in particular we shall attempt to show two important results:

1. For the special case of matrix elements within a given S manifold ($\langle S'M'|\mathcal{H}|SM\rangle$, where $S = S'$), any operator expression containing Δ_i can be replaced by the corresponding expression containing Σ_i if a proportionality constant is applied. This result is particularly important since if $-2J\underline{S}_1\cdot\underline{S}_2$ is much larger than the other terms in $\mathcal{H}$ (a case often encountered experimentally), these are the only matrix elements one needs to evaluate.

2. For matrix elements between spin manifolds ($S'\neq S$), the matrix elements of Δ_i can be evaluated by general formulas that are simple to use, and make possible the identification of zero matrix elements without tedious algebraic manipulations.

II. Irreducible Tensor Operators and The Wigner-Eckhart Theorem.

For much of what will follow, it will be convienient to introduce the irreducible tensor operators. These operators are defined by Racah through the following commutation relationships:

$$[\Sigma_z, T_{lm}(x)] = mT_{lm}(x), \tag{4}$$

$$[\Sigma_{\pm}, T_{lm}(x)] = \{l(l+1)-m(m+1)\}^{1/2}T_{l\pm1,m}(x)$$

where $T_{lm}(x)$ is the $m^{\underline{th}}$ component of an irreducible tensor operator of rank l and operator variable x. The operator variables of interest here are $x = \Sigma, \Delta, S_1$, and S_2. It is also possible to construct irreducible tensor operators of mixed operator variable and for the present case we shall need two such operators of this type, $T_{2m}(S_1S_2)$ and $T_{2m}(\Sigma\Delta)$. In Table I we have collected all of the irreducible tensor operators we shall have need of, and it is easy to show that they do indeed satisfy the commutation relationships in Eq. (4). It can also be seen from Table I that the irreducible tensor operators are nothing more than normalized linear combinations of ordinary cartesian vector operators. A theorem involving irreducible tensor operators that we shall use extensively is the Wigner-Eckart Theorem, which can be expressed as follows:

$$\langle S'M'|T_{lm}(x)|SM\rangle = C(SlS';MmM')\langle S'||T_l(x)||S\rangle. \tag{5}$$

Thus, the Wigner-Eckart theorem states that the matrix elements of an irreducible tensor operator can be decomposed into the product of a Clebsch-Gordan coefficient and a quantity commonly referred to as a reduced matrix element. The Clebsch-Gordan coefficient contains all of the directional or m dependence and is completely independent of the

operator variable, x. The reduced matrix element contains purely dynamical information and is, as the notation implies, completely independent of M', M and m. It is obvious that (5) can be extended to include sums of irreducible tensor operators of the same rank so that we may write formally,

$$\langle S'M'|\sum_m T_{lm}(x)|SM\rangle = \langle S'||T_l(x)||S\rangle \sum_m C(SlS';MmM'). \quad (6)$$

The importance of Eq. (6) lies in the fact that all of the operator expressions that arise from the pair Hamiltonian (Eq. (3)) can be expressed as linear combinations of irreducible tensor operators. To show this is a relatively simple matter which we will illustrate for one of the operators in (3), $\underline{\Delta}\cdot D_\sigma\cdot\underline{\Delta}$.

$$\underline{\Delta}\cdot\underline{D}_\sigma\cdot\underline{\Delta} = \underline{\Delta}\cdot\begin{bmatrix} D_{\sigma xx} & 0 & 0 \\ 0 & D_{\sigma yy} & 0 \\ 0 & 0 & D_{\sigma zz}\end{bmatrix}\cdot\underline{\Delta} =$$

$$\Delta_x^2 D_{\sigma xx} + \Delta_y^2 D_{\sigma yy} + \Delta_z^2 D_{\sigma zz} = (D_{\sigma zz}/2)[3\Delta_z^2 - \Delta\cdot\Delta] + \frac{(D_{\sigma xx}-D_{\sigma yy})}{2}[\Delta_x^2-\Delta_y^2].$$

where use has been made of the fact that D_σ is traceless. Examination of Table I reveals immediately that $[3\Delta_z^2-\underline{\Delta}\cdot\underline{\Delta}] = \sqrt{6}T_{20}(\Delta)$. The second operator requires a bit more work; from ordinary cartesian vector operator algebra we have:

$$[\Delta_x{}^2 - \Delta_y{}^2] = 1/4\,\{(\Delta_+ + \Delta_-)^2 + (\Delta_+ - \Delta_-)^2\} = 1/2(\Delta_+^2 + \Delta_-^2).$$

Upon examination of Table I we see that,

$$1/2(\Delta_+^2 + \Delta_-^2) = T_{22}(\Delta) + T_{2-2}(\Delta).$$

Thus,

$$\underline{\Delta}\cdot\underline{D}_\sigma\cdot\underline{\Delta} = \frac{\sqrt{6}}{2}D_{\sigma zz}T_{20}(\Delta) + \frac{(D_{\sigma xx}-D_{\sigma yy})}{2}[T_{22}(\Delta) + T_{2-2}(\Delta)],$$

where $\underline{D}_{\sigma}$ is in its diagonal representation. If we choose some non-diagonal representation for $\underline{D}_{\sigma}$, the expression for $\underline{\Delta}\cdot\underline{D}_{\sigma}\cdot\underline{\Delta}$ will be more complicated, but it will still prove possible to express it as a linear combination of irreducible tensor operators. All of the operators in Eq. (3) can be treated in a similar manner, and once this is done the Wigner-Eckart theorm (Eqs. 5 and 6) can be used to take matrix elements. We have done this for all operators containing $\underline{\Delta}$, and collected the results in Table II. Many of the operator expressions in Table II will occur only if the interaction tensors are non-diagonal. In order to obtain the equivalent expression for operators involving $\underline{\Sigma}$ one simply replaces Δ by Σ everywhere in the expression.

Table II shows that we have reduced the task of finding the matrix of (3) to finding sums of Clebsh-Gordan coefficients for which standard tables are available[10], and evaluating reduced matrix elements. The reduced matrix elements will be considered in Section III.

An additional expression of interest can be derived by applying Eq. (6) twice, namely:

$$\langle S'M'|\sum_m T_{lm}(x)|SM\rangle=\{\langle S'||T_l(x)||S\rangle/\langle S'||T_l(\Sigma)||S\rangle\}$$
$$\times\langle S'M'|\sum_m T_{lm}(\Sigma)|SM\rangle.$$

However, the above becomes indeterminate for $S \neq S'$ since both $\langle S'M'|\sum_m T_{lm}(\Sigma)|SM\rangle$ and $\langle S'||T_l(\Sigma)||S\rangle$ are zero in this case and thus we are left with the less general expression:

$$\langle SM'|\sum_m T_{lm}(x)|SM\rangle = \left[\frac{\langle S||T_l(x)||S\rangle}{\langle S||T_l(\Sigma)||S\rangle}\right]\times \langle SM'|\sum_m T_{lm}(\Sigma)|SM\rangle. \quad (7)$$

Eq. (7) states that within a given S manifold, the matrix elements of any irreducible tensor operator of operator variable x are proportional to those of the corresponding one with operator variable Σ. The proportionality constant is the ratio of reduced matrix elements and this will be different in general for different S manifolds. We will be interested in two cases, namely $x = \Delta$ and $x = \Sigma\Delta$, and (7) implies that for S'=S elements we shall have no need for Table II since we can make the following operator substitutions:

$$\underline{H}\cdot\underline{G}_\delta\cdot\underline{\Delta} = R^{(s)}\underline{H}\cdot\underline{G}_\delta\cdot\underline{\Sigma}\ ,\ \underline{\Delta}\cdot\underline{D}_\delta\cdot\underline{\Delta} = R'^{(s)}\underline{\Sigma}\cdot\underline{D}_\delta\cdot\underline{\Sigma},$$
$$\underline{\Sigma}\cdot\underline{D}_\delta\cdot\underline{\Delta} = R''^{(s)}\underline{\Sigma}\cdot\underline{D}_\delta\cdot\underline{\Sigma}.$$

where the $R^{(s)}$ are reduced matrix element ratios. The advantage of this is that the matrix elements of operators containing only $\underline{\Sigma}$ are easily evaluated in the coupled representation, and thus once the appropriate reduced matrix element ratios are found we can evaluate any S'=S element with the use of ordinary operator algebra.

III. Reduced Matrix Elements

In order to evaluate the reduced matrix elements in Table II we again use Eq. (5), the Wigner-Eckart Theorm. Then, for $x = \Delta$ we have:

$$\langle S'M'|T_{20}(\Delta)|SM\rangle = C(S2S',M0M')\langle S'||T_2(\Delta)||S\rangle$$

It is easily shown, however, that

$$\langle S'M'|T_{20}(\Delta)|SM\rangle = \langle S'M'|T_{20}(S_1)+T_{20}(S_2)-2T_{20}(S_1S_2)|SM\rangle$$

$$= \langle S'M'|2T_{20}(S_1)+2T_{20}(S_2)-T_{20}(\Sigma)|SM\rangle.$$

Applying (5) to this expression yields

$$<S'M'|T_{20}(\Delta)|SM> = C(S2S';M0M')\{2<S'||T_2(S_1)||S>+2<S'||T_2(S_2)||S> - <S'||T_2(\Sigma)||S>\}.$$

Comparing the two results we find that we have an expression for the reduced matrix elements of $T_2(\Delta)$ in terms of those for $T_2(S_1)$, $T_2(S_2)$, and $T_2(\Sigma)$. This procedure can be applied to the other reduced matrix elements in Table II and the results are given in Eqs. (8).

$$<S'||T_1(\Delta)||S> = <S'||T_1(S_1)||S> - <S'||T_1(S_2)||S> \quad (8a)$$

$$<S'||T_2(\Sigma\Delta)||S> = <S'||T_2(S_1)||S> - <S'||T_2(S_2)||S> \quad (8b)$$

$$<S'||T_2(\Sigma)||S> = 2<S'||T_2(S_1)||S>+2<S'||T_2(S_2)||S>-<S'||T_2(\Sigma)||S> \quad (8c)$$

The advantage of using Eqs. (8) instead of deriving theoretical expressions for $T_l(\Delta)$ and $T_2(\Sigma\Delta)$ directly, is that general expressions for $<S'||T_l(S_1)||S>$ have already been derived (see for instance Reference 2., Rose). For example, it can be shown that,

$$<S'||T_l(S_1)||S> = (-1)^{S_2+l-S_1-S'}[(2S_1+1)(2S+1)]^{1/2}W(SS'S_1S_1;-lS_2)<S_1||T_l(S_1)||S_1>, \quad (9a)$$

where $W(SS'S_1S_1;\ lS_2)$ is the Racah coefficient; standard tables of Racah coefficients similar to those for Clebsh-Gordan coefficients are available[11]. Eq. (9a) then relates the matrix of $T_l(S_1)$ in the coupled representation to its matrix in the uncoupled representation. The expression for $T_l(S_2)$ is:

$$\langle S'||T_l(S_2)||S\rangle = (-1)^{S_1+l-S_2-S}[(2S_2+1)(2S+1)]^{1/2}W(SS'S_2S_2;lS_1)$$
$$\langle S_2||T_l(S_2)||S_2\rangle, \qquad (9b)$$

where the change in phase from (9a) to (9b) can be thought of as arising from permuting the state vectors $|S_2S_1S\rangle$ to their usual form $|S_1S_2S\rangle$.

The remaining reduced matrix elements that must be considered are $\langle S'||T_l(\Sigma)||S\rangle$, $\langle S_i||T_l(S_i)||S_i\rangle$ $(i = 1,2)$. This can be done directly through the Wigner-Eckart Theorm as we shall illustrate for $T_{1m}(\Sigma)$. From Eq. (5) we have,

$$\langle S'||T_1(\Sigma)||S\rangle = \langle S'M'|T_{1m}(\Sigma)|SM\rangle / C(S2S';MmM').$$

Since the l.h.s. must be independent of M',M and m, we choose M' = M, m = 0 and obtain:

$$\langle S'|T_1(\Sigma)||S\rangle = \frac{\langle S'M|T_{10}(\Sigma)|SM\rangle}{C(S1S';MOM)} = \frac{\langle S'M|\Sigma_z|SM\rangle}{C(S1S';MOM)},$$

where use has been made of Table I in the last step. Evaluating the matrix element and using a table of Clebsh-Gordan coefficients we have:

$$\langle S'||T_1(\Sigma)||S\rangle = \frac{\delta_{s's}M}{M/[S(S+1)]^{1/2}} = \delta_{s's}[S(S+1)]^{1/2}.$$

The same procedure can be used to evaluate $\langle S'||T_2(\Sigma)||S\rangle$, $\langle S_1||T_l(S_1)||S_1\rangle$, etc.

We now have expressions for all of the reduced matrix elements of $T_l(S_1)$, $T_l(S_2)$ and $T_l(\Sigma)$, and these yield explicit algebraic formulas through the use of standard tables of Racah and Clabsh-Gordon coefficients; these formulas are collected in Table III. Thus, with the aid of Eq. (8) and Table III we will be able to tabulate explicit expressions for all of the matrix elements in Table II and also to evaluate any reduced matrix element ratio we wish.

IV. The Matrix of the Pair Hamiltonian

From the foregoing it follows that a convenient way to evaluate the matrix of (3) is to consider it as two separate Hamiltonians, one which connects $S' = S$ elements and one for $S' \neq S$ elements. It then follows from (7) that the former will contain only Σ as an electronic spin operator and thus, these matrix elements can be evaluated by the usual operator methods as soon as the proportionality constants in (7) are known. For $S' \neq S$ elements the Spin Hamiltonian will have only those spin operators containing $\underline{\Delta}$ and we will need a separate expression for each such matrix element. The remainder of this paper then will be aimed at illustrating how one goes about using the formalism of the previous sections, and we shall try to do this in such a way, that one may use the formulas without becoming enmeshed in the details that led to them.

A. S'=S Elements

We begin by rewriting (3) entirely in terms of the electronic total spin operator $\underline{\Sigma}$ according to (7) as explained earlier:

$$\mathcal{H}_{S'=S} = -J(\underline{\Sigma}\cdot\underline{\Sigma}-S_1(S_1+1)-S_2(S_2+1)) \tag{11}$$

$$+(\beta/2)\underline{H}\cdot(\underline{G}_\sigma+C\underline{G}_\delta)\cdot\underline{\Sigma}+\left[\frac{(1+C)}{2}\underline{\Sigma}\cdot\underline{A}_1\cdot\underline{I}_1 + \frac{(1-C)}{2}\underline{\Sigma}\cdot\underline{A}_2\cdot\underline{I}_2\right]$$

$$+(1/2)\underline{\Sigma}\cdot\{(1-C_+)\underline{D}_{e+d} + C_+\underline{D}_\sigma+C_-\underline{D}_\delta\}\cdot\Sigma \ .$$

where C and $C_\pm$ are functions of S, S_1 and S_2, and $\underline{\Sigma}$, $\underline{G}_\sigma$, $\underline{G}_\delta$, etc. have been defined below (3). From this it follows that for each of the spin multiplets C and $C_\pm$ will differ, and thus one is using a somewhat different Hamiltonian for each manifold of spin S. The definitions of

these constants in terms of reduced matrix element ratios and explicit algebraic formulas for them are given in Table IV. Otherwise, one uses (11) in the usual manner, with coupled representation state vectors, $|SM\rangle$, as a basis set.

If one considers the case where J is much greater than the other terms in (3) we can consider the properties of the pair as arising from isolated spin multiplets, and use (11) exclusively. Experimentally, this results in a rather interesting e.p.r. spectrum; each multiplet can be thought of as arising from an effective spin Hamiltonian of the form:

$$H = \beta \underline{H} \cdot \underline{G} \cdot \underline{\Sigma} + \underline{\Sigma} \cdot \underline{A}_1 \cdot \underline{I}_1 + \underline{\Sigma} \cdot \underline{A}_2 \cdot \underline{I}_2 + \underline{\Sigma} \cdot \underline{D} \cdot \underline{\Sigma}$$

and in general, these "effective" $\underline{G}$, $\underline{A}$ and $\underline{D}$ tensors will be different for each spin state. These tensors are not, however, independent but are related to the fundemental tensors of the system through the constants in Eq. (11). For $S_1=S_2$, all effective $\underline{G}$ and $\underline{A}$ tensors will be equal to the actual $\underline{G}$ and $\underline{A}$ tensors for all spin states since Table IV reveals that C = 0 in this case. An interesting example of a case where all spin states were observed by e.p.r. has been reported for Cr^{3+} pairs doped in the spinel lattice $MgAl_2O_4$. These authors were able to relate the spectrum of each spin state to the same set of fundamental tensors. Also, they were able to observe the effect of the $\underline{D}_{e+d}$ tensor unobscured by the other possible contributors ($\underline{D}_\sigma$ and $\underline{D}_\delta$) to the "effective" $\underline{D}$ tensor. Examination of Table IV and Eq. (11) shows that for $S_1=S_2=3/2$ this will always be possible since for the S=2 state spectrum $C_+ = C_- = 0$ and thus $\underline{D}_{e+d}$ will be the only fine structure term.

It should be pointed out that other Hamiltonians similar to (11) have been suggested previously. Owen[1] has given a pair Hamiltonian appropriate for the special case $S_1 = S_2$ and all tensors sharing the some major axes. Choa[13] has derived a more general Hamiltonian similar to (11), which in our notation becomes:

$$\begin{aligned} H_S = &-J\{\underline{\Sigma}\cdot\underline{\Sigma}-S_1(S_1+1) - S_2(S_2+1)\}+\beta/2\underline{H}\cdot\{K_1\underline{G}_1 + K_2\underline{G}_2\}\cdot\underline{\Sigma} \\ &+1/2\underline{\Sigma}\cdot\{K_1\underline{A}_1\cdot\underline{I}_1 + K_2\underline{A}_2\cdot\underline{I}_2\}+\underline{\Sigma}\cdot\{1/2\underline{D}_{e+d}-1/2C_1\underline{D}_{e+d}+C_1\underline{D}_1 \\ &+C_2\underline{D}_2-1/2C_2\underline{D}_{e+d}\}\cdot\underline{\Sigma} \end{aligned} \qquad (12)$$

By definition, Choa's constants should be related to ours as follows:

$$C = K_1-1 = 1 - K_2,\ C_{\pm} = 1/2(C_1 \pm C_2). \qquad (13)$$

Using (13) and the expressions below (3) (i.e. $\underline{G}_\sigma = \underline{G}_1 + \underline{G}_2$, $\underline{G}_\delta = \underline{G}_1 - \underline{G}_2$, etc.) one can show that (11) and (12) are in fact identidal. Unfortunately, comparing Table IV with the algebraic formulas in reference 13 reveals that while the definitions involving K_1,K_2 and C in Eq. (13) hold those involving C_1,C_2 and $C_{\pm}$ do not. The error is apparently in Choas expressions for C_1 and C_2 since with these, Eq. (12) gives incorrect matrix elements as compared to either (1) with the expansion in (2) as a basis set or (11) with the $|SM\rangle$ as a basis. The latter two have given identical matrix elements, as they should, for all cases we have checked. Since,

$$C_1 = \frac{\langle S||T_2(S_1)||S\rangle}{\langle S||T_2(\Sigma)||S\rangle} \quad \text{and } C_2 = \frac{\langle S||T_2(S_1)||S\rangle}{\langle S||T_2(\Sigma)||S\rangle},$$

the correct formula for these constants can be found in Table III. It is also worthwhile mentioning that for the special case S_1=S_2, C_+ is identical to the Owen-Judd constant[1] β_S as it should be.

B. S'≠S Elements

As discussed earlier, for these matrix elements, one need only consider operators involving Δ since those not containing this are zero. Eq. (3) then reduces to:

$$\begin{aligned} H_{S'\neq S} &= \beta/2\underline{H}\cdot\underline{G}_\delta\cdot\underline{\Delta} + 1/2\{\underline{\Delta}\cdot\underline{A}_1\cdot\underline{I}_1 - \underline{\Delta}\cdot\underline{A}_2\cdot\underline{I}_2\} \\ &+ 1/4\{\underline{\Delta}\cdot\underline{D}_\sigma\cdot\underline{\Delta}+2\underline{\Sigma}\cdot\underline{D}_\delta\cdot\underline{\Delta}-\underline{\Delta}\cdot\underline{D}_{e+d}\cdot\underline{\Delta}\}. \end{aligned} \tag{14}$$

The matrix elements of all possible operator expressions that can arise from (14) are given in Table V; these formulas result from direct application of the Wigner-Eckart Theorem, Eq. (5). Table V then, is just an explicit form of Table II, and thus, the expression for each matrix element is the product of two quantities: a Clebsch-Gordan coefficient sum and a reduced matrix element. In using (14) one should keep in mind that it is easy to identify the non-zero matrix elements even before Table V is consulted. This follows from two considerations:

1. The two states to be connected must satisfy the triangular relationship with the rank (the l of the $T_{lm}(x)$) of the connecting operator. In (14) we have only first rank ($\underline{H}\cdot\underline{G}_\delta\cdot\underline{\Delta}$, $\underline{\Delta}\cdot\underline{A}_i\cdot\underline{I}_i$) and second rank ($\underline{\Delta}\cdot\underline{D}_\sigma\cdot\underline{\Delta}$, $\underline{\Sigma}\cdot\underline{D}_\delta\cdot\underline{\Delta}$, $\underline{\Delta}\cdot\underline{D}_{e+d}\cdot\underline{\Delta}$) operators. Thus, the former can connect two states only if $S' = S\pm 1$, and the latter only if $S' = S\pm 1$, $S \pm 2$, (disregarding of course $S' = S$ elements which have already been considered). Furthermore, it turns out, that $\underline{\Sigma}\cdot\underline{D}_\delta\cdot\underline{\Delta}$ connects only $S' = S\pm 1$ elements even though it can be expressed as sum of second rank irreducible tensor operators.

2. The operator expressions involving $\Delta_i (i = x, y, z)$ have precisely the same "M" dependence as their Σ_i counter parts. To choose a concrete example, $3\Delta_z^2 - \underline{\Delta} \cdot \underline{\Delta}$ and $3\Sigma_z \Delta_z - \underline{\Sigma} \cdot \underline{\Delta}$ connect only those states where M'=M just like their familiar $3\Sigma_z^2 - \underline{\Sigma} \cdot \underline{\Sigma}$ analog. Similarly $\Delta_x^2 - \Delta_y^2$ and $\Sigma_x \Delta_x - \Sigma_y \Delta_y$ can connect only those states where $M' = M \pm 2$ as is true for $\Sigma_x^2 - \Sigma_y^2$. Knowing the above properties of (14) greatly reduces the number of matrix elements one need consider and it should be noted that most of what has been said in this regard follows immediately from the Wigner-Eckart theorem.

Examination of Table V shows that we have given all of the explicit formulas necessary to determine the unique half of the Hamiltonian matrix for S'≠S elements; *the other half can be found through the relationship*, $\langle S'M'|\mathcal{H}|SM\rangle = \langle SM|\mathcal{H}|S'M'\rangle^*$. To our knowledge this is the first time such formulas have ever been reported. The use of $\underline{\Delta} = \underline{S}_1 - \underline{S}_2$ is not unique here, but has been used occasionally especially in regard to the effect of exchange on spectral linewidths and lineshapes in concentrated magnetic substances.[3,14]

C. Symmetry Considerations

Equations (11) and (14) are completely general and appropriate for any exchange-coupled pair of metal ions irrespective of the relative orientations of the single ion tensors, or the characteristic single ion spins S_1 and S_2. In the case $S_1 = S_2$, it is possible that some crystallographic or approximate symmetry element relates the two ions of the pair. Such symmetry will in some way constrain the form of both (11) and (14) and thus, simplify the problem. The subject of symmetry related tensors has been considered in some detail elsewhere,[15] so will give only a brief

description of how this bears on the pair problem. For what will follow we shall assume that the single ion tensors are real and symmetric; the validity of this assumption is discussed in Abragam and Bleaney's excellent monograph[16]. The following two examples should serve to indicate how one goes about using the symmetry of the pair to advantage. Let us represent some symmetry related pair of tensors for the system (for the present case, the pairs $\underline{G}_1,\underline{G}_2$, $\underline{A}_1,\underline{A}_2$ and $\underline{D}_1,\underline{D}_2$ are of interest) as $\underline{B}_1,\underline{B}_2$. We will write these as 3x3 matrices of the general form

$$\underline{B}_i = \begin{pmatrix} B_{ixx} & B_{ixy} & B_{ixz} \\ B_{ixy} & B_{iyy} & B_{iyz} \\ B_{ixz} & B_{iyz} & B_{izz} \end{pmatrix}, \quad i = 1,2.$$

Furthermore, let the principal values of B_i be β_{ixx}, β_{iyy}, β_{izz}, and call the coordinate system that makes $\underline{B}_i$ diagonal (the major axis system of B_i) the x_i, y_i, z_i system, $i = 1,2$. Since $\underline{B}_1$ is related to $\underline{B}_2$ by some symmetry element, the principal values of both will be identical, (i.e., $\beta_{1jj} = \beta_{2jj}$, (i, j = x,y,z)), but it will not necessarily be true that $\underline{B}_1=\underline{B}_2$ when the two are referred to some common coordinate system. Instead, they will be related by the transformation equation:

$$\underline{R}^{-1}\underline{B}_1\underline{R} = \underline{B}_2, \qquad (15)$$

where $\underline{R}$ is the matrix that represents a symmetry element relating the pair. We will now consider two examples in order to illustrate how (15) restricts the form of (11) and (14).

<u>$C_i(\bar{1})$ Symmetry</u>

From (15) we have:

$$\underline{i}^{-1} B_1 \underline{i} = B_2,$$

where i is the inversion matrix. Without loss of generality we may write this in the following explicit form:

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}^{-1} \begin{pmatrix} B_{1xx} & B_{1xy} & B_{1xz} \\ B_{1xy} & B_{1yy} & B_{1yz} \\ B_{1xz} & B_{1yz} & B_{1zz} \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} B_{2xx} & B_{2xy} & B_{2xz} \\ B_{2xy} & B_{2yy} & B_{2yz} \\ B_{2xz} & B_{2yz} & B_{2zz} \end{pmatrix}$$

Upon performing the matrix multiplication we have:

$$\begin{pmatrix} B_{1xx} & B_{1xy} & B_{1xz} \\ B_{1xy} & B_{1yy} & B_{1zz} \\ B_{1xz} & B_{1yz} & B_{1zz} \end{pmatrix} = \begin{pmatrix} B_{2xx} & B_{2xy} & B_{2xz} \\ B_{2xy} & B_{2yy} & B_{2yz} \\ B_{2xz} & B_{2yz} & B_{2zz} \end{pmatrix}. \qquad (16)$$

Eq. (16) reveals that in any arbitrary coordinate system, $B_{1ij} = B_{2ij}$ (i,j, = xyz) and this restricts (11) and (14) as follows:

(a) The difference tensors $\underline{G}_\delta$ and $\underline{D}_\delta$ are zero.

(b) The sum tensors $\underline{G}_\sigma$ and $\underline{D}_\sigma$ are simply twice the single ion tensors.

(c) From (16) it follows that the x_1, y_1, z_1 system is identical in orientation to the x_2, y_2, z_2 system and also to the major axis system of sum tensors.

Thus, once the tensors of the pair are determined experimentally one has also determined the single ion tensors as well; we will see later that this is not always possible. Also, is <u>not</u> possible in this case to tell how the major axes of the tensors are related to the geometry of the pair, nor can we restrict the major axes of $\underline{D}_{e+d}$ to be the same as those for the other tensors in Eqs. (11) and (14).

<u>D_2(222) Symmetry</u>

For this case we have three mutually perpendicular two-folds, two of which relate the two ions of the pair, the third being colinear with the line joining the two ions of the pair. Let these symmetry axes define the x, y, z system and we will arbitrarily choose to call the direction of the line joining the two ions z. Any other choice for this direction amounts to a simple relabeling of axes. Eq. (15) now gives us the following two expressions:

$$\underline{C}_{2x}^{-1}\,\underline{B}_1\underline{C}_{2x} = \underline{B}_2, \quad \underline{C}_{2y}^{-1}\,\underline{B}_1\,\underline{C}_{2y} = \underline{B}_2,$$

where $\underline{C}_{2i}$ represents a rotation of 180° around two-fold parallel to the $i = x,y$ direction. Performing the matrix multiplication yields:

$$\begin{pmatrix} B_{1xx} & -B_{1xy} & -B_{1xz} \\ -B_{1xy} & B_{1yy} & B_{1yz} \\ -B_{1xz} & B_{1yz} & B_{1zz} \end{pmatrix} = \begin{pmatrix} B_{2xx} & B_{2xy} & B_{2xz} \\ B_{2xy} & B_{2yy} & B_{2yz} \\ B_{2xz} & B_{2yz} & B_{2zz} \end{pmatrix},$$

$$\begin{pmatrix} B_{1xx} & -B_{1xy} & B_{1xz} \\ -B_{1xy} & B_{1yy} & B_{1yz} \\ B_{1xz} & -B_{1yz} & B_{1zz} \end{pmatrix} = \begin{pmatrix} B_{2xx} & B_{2xy} & B_{2xz} \\ B_{2xy} & B_{2yy} & B_{2yz} \\ B_{2xz} & B_{2yz} & B_{2zz} \end{pmatrix}.$$

In order for both of the above to be true the following must also be true: $B_{1xz} = B_{2xz} = 0$, $B_{1yz} = B_{2yz} = 0$. With this, the content of the above two matrix equations can be expressed as follows,

$$\begin{pmatrix} B_{1xx} & -B_{1xy} & 0 \\ -B_{1xy} & B_{1yy} & 0 \\ 0 & 0 & B_{1zz} \end{pmatrix} = \begin{pmatrix} B_{2xx} & B_{2xy} & 0 \\ B_{2xy} & B_{2yy} & 0 \\ 0 & 0 & B_{2zz} \end{pmatrix}, \qquad (17)$$

and (17) implies then that z_1, z_2 and z are all colinear, that is, the two single ion tensor share a common major axis. Eq. (17) restricts the sum and difference tensors to the following explicit form:

$$\underline{B}_\sigma = \begin{pmatrix} 2B_{1xx} & 0 & 0 \\ 0 & 2B_{1yy} & 0 \\ 0 & 0 & 2B_{1zz} \end{pmatrix} \quad \underline{B}_\delta = \begin{pmatrix} 0 & -2B_{1xy} & 0 \\ -2B_{1xy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} . \quad (18)$$

We have thus obtained a great deal of information about how the major axes of the tensors are related to the geometry of the pair. It is also possible to obtain some further information about the single ion tensor themselves. Since both B_1 and B_2 share z as a major axis, it follows that a rotation around z will be sufficient to make x_1, colinear with x and y_1 colinear with y. If we call the angle needed to do this θ, the corresponding angle for x_2 and y_2 is $-\theta$. In terms of its principal values the form of B_1 in the xyz system becomes:

$$\underline{B}_1 = \begin{bmatrix} [\beta_{1xx}\cos^2\theta+\beta_{1yy}\sin^2\theta] & [\beta_{1xx}-\beta_{1yy}]\sin\theta\cos\theta & 0 \\ [\beta_{1xx}-\beta_{1yy}]\sin\theta\cos\theta & [\beta_{1yy}\cos^2\theta+\beta_{1xx}\sin^2\theta] & 0 \\ 0 & 0 & \beta_{1zz} \end{bmatrix} . \quad (19)$$

The corresponding expression for B_2 can be found by replacing θ by $-\theta$ and 1 by 2 everywhere in (19). Equation (19) then gives explicit expressions for the B_{1ij} and B_{2ij} of (17) and (18) in terms of their principal values and the angle θ. Thus, if one were to determine experimentally all the sum and difference tensors contained in (11) and (14), one could also find the principal values of the single ion tensors as well as the angle θ. This is not always possible, and to see this, consider the common experimental case where J is much greater than the other terms in

the pair Hamiltonian. We thus ignore the inter-multiplet matrix elements and use only Eq. (11) to describe the pair. Examination of Table IV reveals that for $S_1=S_2$ the coefficients of $\underline{G}_\delta$ and $\underline{D}_\delta$ which are C and C_- respectively, are both zero for all multiplets. It then follows that all the observable information about the single ion $\underline{G}$ and $\underline{D}$ tensors is contained in $\underline{G}_\sigma$ and $\underline{D}_\sigma$ which from (17), (18) and (19) have the following form:

$$\underline{B}_\sigma = 2\begin{bmatrix} [\beta_{1xx}\cos^2\theta+\beta_{1yy}\sin^2\theta] & 0 & 0 \\ 0 & [\beta_{1xx}\sin^2\theta+\beta_{1yy}\cos^2\theta] & 0 \\ 0 & 0 & \beta_{1zz} \end{bmatrix}. \quad (20)$$

From (20), it is clear that even after the sum tensors are found there will be only three equations for the four unknowns to be determined. Thus, unlike the situation in $C_i(\bar{1})$ symmetry, determination of all the "observable" information in the pair spectra will not in general be sufficient to completely describe the single ions when the pair symmetry is $D_2(222)$.

ACKNOWLEDGEMENT

We wish to thank Professor Gerald Kokoszka for his helpful comments on this manuscript. The research was supported in part by the Office of Naval Research.

REFERENCES

[1] J. Owen, 1971, J. Appl. Phys., 32, 213S.

[2] J. Owen, 1962, J. Appl. Phys., 33, 355.

[3] Kokoszka, G.F. and Gordon, G, 1969, Transition Metal Chem., 5, 181.

[4] Kokoszka, G.F., and Duerst, R.W., 1970, Coord. Chem. Rev., 5, 209.

[5] Sinn, E., 1970, Coord. Chem. Rev., 5, 313.

[6] Hodgson, D.J., 1974, Prog. Inorg. Chem., 19, 173.

[7] Hatfield, W.E., "Theory and Applications of Molecular Paramagnetism", E.A. Boudreaux and L.N. Mulay, Editors, John Wiley & Sons, Chapter VII, 1976.

[8] LaMar, G.N., Eaton, G.R., Holm, R.H., and Walker, F.A., 1973, J. Amer. Chem. Soc., 95, 63, and references therein.

[9] Rose, M.E., *Elementary Theory of Angular Momentum*, John Wiley and Sons, Inc., 1967.

[10] Condon, E.U., and Shortley, G.H., *Theory of Atomic Spectra*, Cambridge University Press, 1935.

[11] Biedenharn, L.C., Blatt, J.M., and Rose, M.E., 1952, Rev. Mod. Phys., 24, 249.

[12] Henning, J.C.M., and van den Boom, H., 1973, Phys. Rev. B,8, 2255.

[13] Choa, C.C., 1973, J. Mag. Res., 10, 1.

[14] Beswick, J.R. and Dugdale, D.E., 1973, J. Phys., C,6, 3326.

[15] Weil, J.A., Buck, T., and Clapp, J.E., 1973, Adv. Mag. Res., 6, 183.

[16] Abragam, A, and Bleaney, B.,"Electron Paramagnetic Resonance of Transition Ions", Clarendon Press - Oxford, 1970, pgs. 750 ff.

Table I

Some Irreducible Tensor Operators*

$T_{10}(\Delta) = \Delta_z,\ T_{11}(\Delta) = -1/\sqrt{2}\Delta_+,\ T_{1,-1} = 1/\sqrt{2}\Delta.$

$T_{22}(\Delta) = 1/2\Delta_+^2$

$T_{21}(\Delta) = -1/2[\Delta_z\Delta_+ + \Delta_+\Delta_z]$

$T_{20}(\Delta) = 1/\sqrt{6}[3\Delta_z^2 - \underline{\Delta}\cdot\underline{\Delta}]$

$T_{2,-1}(\Delta) = 1/2[\Delta_z\Delta_- - \Delta_-\Delta_z]$

$T_{2,-2}(\Delta) = 1/2\Delta_-^2$

$T_{22}(\Sigma\Delta) = 1/2[\Sigma_+\Delta_+]$

$T_{21}(\Sigma\Delta) = -1/2[\Sigma_z\Delta_+ + \Sigma_+\Delta_z]$

$T_{20}(\Sigma\Delta) = 1/\sqrt{6}[3\Sigma_z\Delta_z - \underline{\Sigma}\cdot\underline{\Delta}]$

$T_{2,-1}(\Sigma\Delta) = 1/2[\Sigma_z\Delta_- + \Sigma_-\Delta_z]$

$T_{2,2}(\Sigma\Delta) = 1/2[\Sigma_-\Delta_-]$

$T_{22}(S_1S_2) = 1/2[S_{1+}S_{2+}]$

$T_{21}(S_1S_2) = -1/2[S_{1z}S_{2+} + S_{1+}S_{2z}]$

$T_{20}(S_1S_2) = 1/\sqrt{6}[3S_{1z}S_{2z} - S_1\cdot S_2]$

$T_{2,1}(S_1S_2) = 1/2\ [S_{1z}S_{2-} + S_{1-}S_{2z}]$

$T_{2,-2}(S_1S_2) = 1/2[S_{1-}S_{2-}]$

*To find $T_{\ell m}(x)$ with $x = \Sigma,\ S_1,\ S_2$ replace Δ above by desired operator variable.

Table II

Matrix Elements by the Wigner-Eckhart Theorem

$\langle S'M'\vert\Delta_z\vert SM\rangle$	$C(S\,S';M0M)$	$\times\langle S'\vert\vert T_1(\Delta)\vert\vert S\rangle$
$\langle S'M'\vert\Delta_x\vert SM\rangle$	$\sqrt{2}/2[C(S1S';M\text{-}1M')-C(S1S';M1M')]$	$\times\langle S'\vert\vert T_1(\Delta)\vert\vert S\rangle$
$\langle S'M'\vert\Delta_y\vert SM\rangle$	$-i\sqrt{2}/2[C(S1S';M\text{-}1M')+C(S1S';M1M']$	$\times\langle S'\vert\vert T_1(\Delta)\vert\vert S\rangle$
$\langle S'M'\vert 3\Sigma_z\Delta_z-\underline{\Sigma}\cdot\underline{\Delta}\vert SM\rangle$	$\sqrt{6}C(S2S';M0M')$	$\times\langle S'\vert\vert T_2(\Sigma\Delta)\vert\vert S\rangle$
$\langle S'M'\vert\Sigma_x\Delta_z-\Sigma_x\Delta_z\vert SM\rangle$	$[C(S2S';M\text{-}1M')-C(S2S';M1M')]$	$\times\langle S'\vert\vert T_2(\Sigma\Delta)\vert\vert S\rangle$
$\langle S'M'\vert\Sigma_y\Delta_z+\Sigma_z\Delta_y\vert SM\rangle$	$i[C(S2S';M\text{-}1M')+C(S2S';M1M')]$	$\times\langle S'\vert\vert T_2(\Sigma\Delta)\vert\vert S\rangle$
$\langle S'M'\vert\Sigma_x\Delta_x-\Sigma_y\Delta_y\vert SM\rangle$	$[C(S2S';M\text{-}2M')+C(S2S';M2M')]$	$\times\langle S'\vert\vert T_2(\Sigma\Delta)\vert\vert S\rangle$
$\langle S'M'\vert\Sigma_u\Delta_x-\Sigma_x\Delta_y\vert SM\rangle$	$i[C(S2S';M\text{-}2M')+C(S2S';M2M')]$	$\times\langle S'\vert\vert T_2(\Sigma\Delta)\vert\vert S\rangle$
$\langle S'M'\vert 3\Delta_z^2-\underline{\Delta}\cdot\underline{\Delta}\vert SM\rangle$	$\sqrt{6}C(S2S';M0M')$	$\times\langle S'\vert\vert T_2(\Delta)\vert\vert S\rangle$
$\langle S'M'\vert\Delta_x\Delta_z+\Delta_z\Delta_x\vert SM\rangle$	$[C(S2S';M\text{-}1M')-C(S2S';M1M')]$	$\times\langle S'\vert\vert T_2(\Delta)\vert\vert S\rangle$
$\langle S'M'\vert\Delta_y\Delta_z+\Delta_z\Delta_y\vert SM\rangle$	$i[C(S2S';M\text{-}1M')-C(S2S';M1M')$	$\times\langle S'\vert\vert T_2(\Delta)\vert\vert S\rangle$
$\langle S'M'\vert\Delta_x^2-\Delta_y^2\vert SM\rangle$	$[C(S2S';M\text{-}2M')+C(S2S';M2M')]$	$\times\langle S'\vert\vert T_2(\Delta)\vert\vert S\rangle$
$\langle S'M'\vert\Delta_x\Delta_y-\Delta_y\Delta_x\vert SM\rangle$	$i[C(S2S';M\text{-}2M')-C(S2S';M2M')]$	$\times\langle S'\vert\vert T_2(\Delta)\vert\vert S\rangle$

Table III.

Reduced Matrix Elements of $T_{1m}(\Sigma)$ and $T_{1m}(S_i)$

$$\langle S' || T_1(\Sigma) || S \rangle = \delta_{SS'} \sqrt{S(S+1)}$$

$$\langle S_i' || T_1(S_i) || S \rangle = \delta_{S_i' S_i} \sqrt{S_i(S_i+1)}$$

$$\langle S' || T_2(\Sigma) || S \rangle = \delta_{S'S} \sqrt{(2S+3)(2S-1)S(S+1)/6}$$

$$\langle S_i || T_2(S_i) || S_i \rangle = \delta_{S'S} \sqrt{(2S_i+3)(2S_i-1)S_i(S_i+1)/6}$$

Table III

(Reduced Matrix Elements* Continued)

$$\langle S\|T_1(S_1)\|S\rangle/\langle S\|T_1(\Sigma)\|S\rangle = 1/2\{S(S+1)+S_1(S_1+1)-S_2(S_2+1)\}/S(S+1)$$

$$\langle S\|T_1(S_2)\|S\rangle/\langle S\|T_1(\Sigma)\|S\rangle = 1/2\{S(S+1)+S_2(S_2+1)-S_1(S_1+1)\}/S(S+1)$$

$$\langle S\|T_2(S_1)\|S\rangle/\langle S\|T_2(\Sigma)\|S\rangle = \frac{3[S_2(S_2+1)-S_1(S_1+1)-S(S+1)]^2+3[S_2(S_2+1)-S_1(S_1+1)-S(S+1)]-4S(S+1)S_1(S_1+1)}{2(2S+3)(2S-1)S(S+1)}$$

$$\langle S\|T_2(S_2)\|S\rangle/\langle S\|T_2(\Sigma)\|S\rangle = \frac{3[S_1(S_1+1)-S_2(S_2+1)-S(S+1)]^2+3[S_1(S_1+1)-S_2(S_2+1)-S(S+1)]-4S(S+1)S_1(S_1+1)}{2(2S+3)(2S-1)S(S+1)}$$

$$\langle S+1\|T_1(S_1)\|S\rangle = -\langle S+1\|T_1(S_2)\|S\rangle = 1/2\{(S_1+S_2+S+2)(S_1-S_2+S+1)(S_2-S_1+S+1)(S_1+S_2-S)/(2S+3)(S+1)\}^{1/2}$$

$$\langle S+1\|T_2(S_1)\|S\rangle = 1/2\left\{\frac{(S_1+S_2+S+2)(S_1+S_2-S)(S_1-S_2+S+1)(S_2-S_1+S+1)}{(2S+4)(2S+3)S(S+1)}\right\}^{1/2}\cdot[S(S+2)+S_1(S_1+1)-S_2(S_2+1)]$$

$$\langle S+1\|T_2(S_2)\|S\rangle = -1/2\left\{\frac{(S_1+S_2+S+2)(S_1+S_2-S)(S_1-S_2+S+1)(S_2-S_1+S+1)}{(2S+4)(2S+3)S(S+1)}\right\}^{1/2}\cdot[S(S+2)+S_2(S_2+1)-S_1(S_1+1)$$

$$\langle S+2\|T_2(S_1)\|S\rangle = \langle S+2\|T_2(S_2)\|S\rangle = 1/2\left[\frac{(S_1+S_2+S+3)(S_1+S_2+S+2)(S_1-S_2+S+2)(S_2-S_1+S+2)(S_1-S_2+S+1)(S_2-S_1+S+1)(S_1+S_2-S)(S_1+S_2-S-1)}{(2S+5)(2S+4)(2S+3)(2S+2)}\right]^{1/2}$$

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*If the substitution S=0 makes a reduced matrix element indeterminate, the expression is equal to zero.

Table IV

A. Constants for Eq. (11)*

$$C = \frac{\langle S||T_1(\Delta)||S\rangle}{\langle S||T_1(\Sigma)||S\rangle} = \frac{S_1(S_1+1)-S_2(S_2+1)}{S(S+1)}$$

$$C_+ = 1/2\{\frac{\langle S||T_2(\Delta)||S\rangle}{\langle S||T_2(\Sigma)||S\rangle} + 1\}$$

$$= \frac{\{3[S_1(S_1+1)-S_2(S_2+1)]^2+S(S+1)[3S(S+1)-3-2S_1(S_1+1)-2S_2(S_2+1)]\}}{[(2S+3)(2S-1)S(S+1)]}$$

$$C_- = \frac{\langle S||T_2(\Sigma\Delta)||S\rangle}{\langle S||T_2(\Sigma)||S\rangle} = \frac{\{S(S+1)[S_1(S_1+1)-S_2(S_2+1)]\}-3[S_1(S_1+1)-S_2(S_2+1)]}{(2S+3)(2S-1)S(S+1)}$$

*C, $C_{\pm} = 0$ for $S = 0$.

Table
IV B. Matrix Elements of Operators Containing Δ for $S' \neq S$ in Coupled Representation for use with Eq. (14)*

$$\left.\begin{aligned}
\langle S+1, M|\Delta_z|S, M\rangle &= \left\{\frac{(S-M+1)(S+M+1)}{(2S+1)(S+1)}\right\}^{1/2} \\
\langle S+1, M\pm 1|\Delta_x|S, M\rangle &= \mp 1/2\left\{\frac{(S\pm M+1)(S\pm M+2)}{(2S+1)(S+1)}\right\}^{1/2} \\
\langle S+1, M\pm 1|\Delta_y|S, M\rangle &= -i/2\left\{\frac{(S\pm M+1)(S\pm M+2)}{(2S+1)(S+1)}\right\}^{1/2}
\end{aligned}\right] \times\left\{\frac{(S_1+S_2+S+2)(S_1-S_2+S+1)(S_2-S_1+S+1)(S_1+S_2-S)}{(2S+3)(S+1)}\right\}^{1/2}$$

$$\left.\begin{aligned}
\langle S+1, M|3\Sigma_z\Delta_z - \Sigma\,\Delta|SM\rangle &= \sqrt{6}(M)\left\{\frac{3(S-M+1)(S+M+1)}{S(S+1)(2S+1)}\right\}^{1/2} \\
\langle S+1, M\pm 1|\Sigma_x\Delta_z+\Sigma_z\Delta_x|SM\rangle &= (S\pm 2M)\left\{\frac{(S\pm M+2)(S\pm M+1)}{2S(S+1)(2S+1)(S+2)}\right\}^{1/2} \\
\langle S+1, M\pm 1|\Sigma_y\Delta_z+\Sigma_z\Delta_y|SM\rangle &= \mp i(S\pm 2M)\left\{\frac{(S\pm M+2)(S\pm M+1)}{2S(S+1)(2S+1)(S+2)}\right\}^{1/2} \\
\langle S+1, M\pm 2|\Sigma_x\Delta_x-\Sigma_y\Delta_y|SM\rangle &= \mp\left\{\frac{(S\pm M+1)(S\pm M+2)(S\pm M+3)(S\mp M)}{2S(S+1)(2S+1)(S+2)}\right\}^{1/2} \\
\langle S+1, M\pm 2|\Sigma_x\Delta_y+\Sigma_y\Delta_x|SM\rangle &= i\left\{\frac{(S\pm M+1)(S\pm M+2)(S\pm M+3)(S\mp M)}{2S(S+1)(2S+1)(S+2)}\right\}^{1/2}
\end{aligned}\right] \times\left\{\frac{(S_1+S_2+S+2)(S_1+S_2-S)(S_1-S_2+S+1)(S_2-S_1+S+1)(S+2)}{(2S+3)(2S+2)}\right\}^{1/2}$$

(Table IV B. Con't.)

$$\langle S+1,M|3\Delta_z^2-\underline{\Delta}\cdot\underline{\Delta}|S,M\rangle = \sqrt{6}(M)\left\{\frac{3(S-M+1)(S+M+1)}{S(S+1)(2S+1)(S+2)}\right\}^{1/2}$$

$$S+1,M\pm1|\Delta_x\Delta_z+\Delta_z\Delta_x|S,M\rangle = (S\mp2M)\left\{\frac{(S\pm M+2)(S\pm M+1)}{2S(S+1)(2S+1)(S+2)}\right\}^{1/2}$$

$$\langle S+1,M\pm1|\Delta_y\Delta_z+\Delta_z\Delta_y|SM\rangle = \mp i(S\mp2M)\left\{\frac{(S\pm M+2)(S\pm M+1)}{2S(S+1)(2S+1)(S+2)}\right\}^{1/2}$$

$$\langle S+1,M\pm2|\Delta_x^2-\Delta_y^2|SM\rangle = \mp\left\{\frac{(S\mp M)(S\pm M+1)(S\pm M+2)(S\pm M+3)}{2S(S+1)(S+2)(2S+1)}\right\}^{1/2}$$

$$\langle S+1,M\pm2|\Delta_x\Delta_y+\Delta_y\Delta_x|SM\rangle = i\left\{\frac{(S\mp M)(S\pm M+1)(S\pm M+2)(S\pm M+3)}{2S(S+1)(S+2)(2S+1)}\right\}^{1/2}$$

$$\times\ 2\left\{\frac{(S_1+S_2+S+2)(S_1+S_2-S)(S_1-S_2+S+1)(S_2-S_1+S+1)}{(2S+4)(2S+3)S(S+1)}\right\}^{1/2} \times$$

$$\{S_1(S_1+1)-S_2(S_2+1)\}$$

$$\langle S+2,M|3\Delta_z^2-\underline{\Delta}\cdot\underline{\Delta}|SM\rangle = \sqrt{6}\left\{\frac{3(S-M+2)(S-M+1)(S+M+2)(S+M+1)}{(2S+1)(2S+2)(2S+3)(S+2)}\right\}^{1/2}$$

$$\langle S+2,M\pm1|\Delta_x\Delta_z+\Delta_z\Delta_x|S,M\rangle = \mp\left\{\frac{(S\mp M+1)(S\pm M+3)(S\pm M+2)(S\pm M+1)}{(2S+1)(S+1)(2S+3)(S+2)}\right\}^{1/2}$$

$$\langle S+2,M\pm1|\Delta_y\Delta_z+\Delta_z\Delta_y|S,M\rangle = \mp i\left\{\frac{(S\mp M+1)(S\pm M+3)(S\pm M+2)(S\pm M+1)}{(2S+1)(S+1)(2S+3)(S+2)}\right\}^{1/2}$$

$$\langle S+2,M\pm2|\Delta_x^2-\Delta_y^2|SM\rangle = \left\{\frac{(S\pm M+1)(S\pm M+2)(S\pm M+3)(S\pm M+4)}{(2S+1)(2S+2)(2S+3)(2S+4)}\right\}^{1/2}$$

$$\langle S+2,M\pm2|\Delta_x\Delta_y+\Delta_y\Delta_x|SM\rangle = \mp i\left\{\frac{(S\pm M+1)(S\pm M+2)(S\pm M+3)(S\pm M+4)}{(2S+1)(2S+2)(2S+3)(2S+4)}\right\}^{1/2}$$

$$\times 2\left\{\frac{(S_1+S_2+S+3)(S_1+S_2+S+2)(S_1-S_2+S+2)(S_1-S_2+S+1)\times(S_2-S_1+S+2)(S_2-S_1+S+1)(S_1+S_2-S)(S_1+S_2-S-1)}{(2S+5)(2S+4)(2S+3)(2S+2)}\right\}^{1/2}$$

*If the substitution S=0 makes a matrix element indeterminate, the expression is equal to zero.